Name: KEY SID:

Discussion Section: (Deborah, Heidi, Josh)

1. (20 pts) When sheep eat wet alfalfa, a chemical reaction takes place which causes froth to build up in their rumen. The result of this froth is that gas produced in the rumen cannot be released by normal means—for all intents and purposes, the rumen acts as a closed system. The condition is called "pasture bloat" because the build up of gases literally causes the sheep to expand. If pasture bloat is not immediately dealt with, it can be fatal to the sheep.

(a) Sharon the Sheep's rumen contains some digestive juices and a small amount of gas. If the pressure of CO_2 above the digestive juices in her rumen is measured at 0.1 atm, what is the concentration of CO_2 in her digestive juices? K_{CO2}= 1.41 x 10^3 atm at 37 ° C (sheep temperature) in digestive juices.

$P_{CO_2} = k_{CO_2} X_{CO_2}$ (+2) right equation

$X_{CO_2} = \underbrace{\frac{P_{CO_2}}{k_{CO_2}} = \frac{0.1\,\text{atm}}{1.41\times10^3\,\text{atm}}}_{\text{(+1) set up to solve}} = 7.09\times10^{-5}$ (+1) getting the right answer

$c_{CO_2} = (7.09\times10^{-5})(55.6\text{ M}) = \boxed{3.94\times10^{-3}\text{ M}}$

answers in molarity or mole fraction are accepted

4 points total

(b) After eating wet alfalfa, Sharon develops pasture bloat. At this point, her rumen contains 1L of stomach juices and 100 mL of vapor. If 1.0 moles of CO_2 build up in her rumen, what are P_{CO2}, the pressure of carbon dioxide above the juices, and c_{CO2}, the concentration in the juices? Assume that the carbon dioxide gas acts ideally, and that the rumen doesn't expand any further.

$n_{air} \equiv$ # of moles in vapor of CO_2

$n_{juices} \equiv$ # of moles in juices of CO_2

$n_{air} + n_{juices} = 1.0$ moles (+1) conservation condition

$P_{CO_2} = k_{CO_2} X_{CO_2}$ (+1) right equation

$\frac{n_{air}RT}{V} = k_{CO_2}\left(\frac{n_{juices}}{55.6}\right) = k_{CO_2}\left(\frac{1.0 - n_{air}}{55.6}\right)$

(+1) using $P = \frac{nRT}{V}$ (+2) plugging in right values

$$\frac{n_{air}(.08205\,\frac{\text{L}\cdot\text{atm}}{\text{mol K}})(310\text{K})}{(.1\text{ L})} = \frac{1.41\times10^3\text{ atm}}{55.6\text{ moles}}(1.0 - n_{air})$$

$254 \cdot n_{air} = 25.4(1 - n_{air})$

$279.8\, n_{air} = 25.4$

$n_{air} = 9.09\times10^{-2}$ moles (+1) right value

$$P_{CO_2} = \frac{(9.09\times10^{-2}\text{ mol})(.08206\,\frac{\text{L}\cdot\text{atm}}{\text{mol K}})(310)}{(.10\text{ L})} = \boxed{23.1\text{ atm}}$$ (+1) right pressure

$$c_{CO_2} = \frac{1 - 9.09\times10^{-2}}{1\text{ L}} = \boxed{9.09\times10^{-1}\text{ M}}$$ (+1) right concentration

(+4) if you assume it's all in liquid or all in vapor

8 points total

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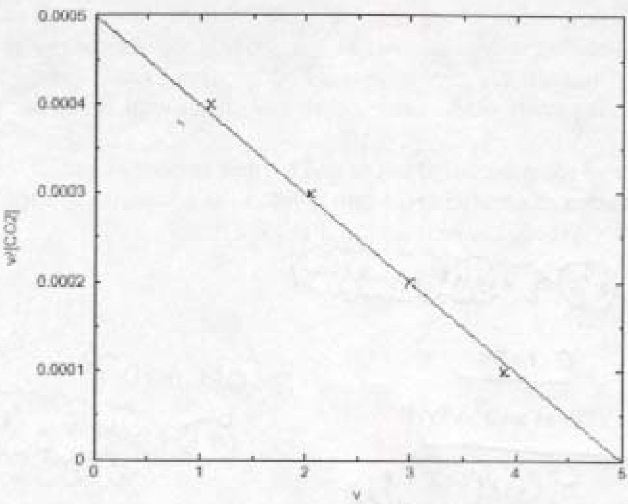
(c) A pharmaceutical company claims to have developed a drug that can stop pasture bloat. This drug is a macromolecule that binds CO_2. To demonstrate its effectiveness, they provide the following data plot:



Determine the number of binding sites per macromolecule and the intrinsic binding constant. Do you think that this drug will work?

N = x-intercept = $\underline{5}$

4pts total

NK_B = y intercept = 0.0005

(+3) right values of N and K

$\Rightarrow \quad K_0 = \dfrac{0.0005}{5} = \underline{1.0 \times 10^{-4}}$

No, the drug will not work because it binds very little CO_2!

(+1) explanation

(d) Suggest another method that might be used to either prevent or cure pasture bloat, and briefly explain why it might work. Use arguments from biophysical chemistry to support your statements. Do not exceed three sentences.

The following methods are acceptable: (+3) reasonable cure/prevention (+1) explanation

(1) Puncture the rumen. This alleviates the excess pressure. Suture it back up.

(2) Do not feed sheep wet alfalfa. For the reaction wet alfalfa $\rightarrow$ foam, $\Delta G = \Delta G^\circ + RT \ln\left(\frac{\text{products}}{\text{reactants}}\right)$, if wet alfalfa (products) is 0, $\Delta G = +\infty$ so no foam is formed.

(3) Feed sheep a surfactant. This breaks up the foam, allowing gas to be expelled.

(4) Agitate the sheep. This allows gas bubbles to break through the foam, thus stopping dangerous gas build up.

$\boxed{\text{METHODS 1–4 ARE ACTUALLY USED BY FARMERS}}$

—continued—

OTHER ANSWERS ACCEPTED FOR 1d)

(1) Decrease temperature of sheep. This increases solubility of CO_2, so high pressures do not build up.
(Not used by farmers since this is bad for the sheep).

(2) Put sheep in pressure chamber. This will stop expansion of rumen.
(Also bad for sheep).

(3) Use a macromolecule with a higher binding constant/ more cooperativity.
(Probably doesn't exist).

(4) Add solvent to rumen in which CO_2 is very soluble, reducing CO_2 (g).
(Not used since solvents are poisonous).

etc....

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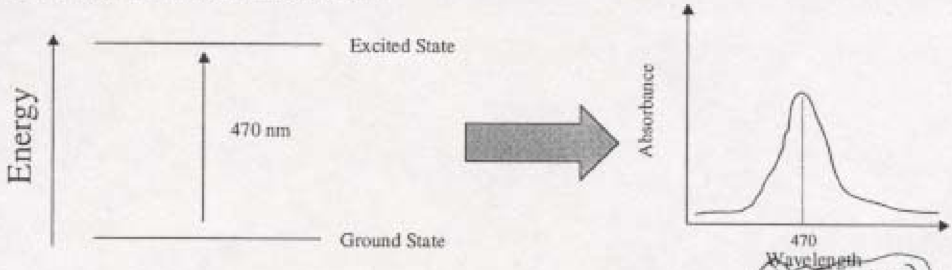
2. (12 pts) Carotenoids, the orange and red pigments common in carrots, spinach and tomatoes, play a strong role in protecting organisms from UV light by absorbing it. We are most familiar with carotenoids in the form of vitamin A. A scientist has discovered a new carotenoid in spinach leaves. The pigment (known as pigment Z) is a single molecule that absorbs light at a wavelength of 470 nm (6.38×10^{15} Hz) thus transitioning from the non-degenerate ground state to a single, non-degenerate excited state. You might need h= 6.626×10^{-34} Js. For these problems assume these are the only two states in the system.

Define:

ground state = 0



(+1) $E = h\nu$

(a) A researcher wishes to perform experiments upon the excited state pigment Z molecules. However, his main laser light source, which he would normally utilize to excite the pigment Z molecules, caught on fire and doesn't work. At a temperature of 25 degrees C, will he be able to have a good chance at observing the excited state molecules? Explain why (don't be afraid to show some calculation!)

$$P(\text{excited State}) \propto e^{-\frac{E_{es}}{kT}} = e^{-\frac{(6.626\times10^{-34})(6.38\times10^{15})}{(1.380\times10^{-23})(298)}} = 3.22\times10^{-465}$$

(+1) right eqn (+1) answer

4

Since the normalization constant is greater than 1, the probability of an excited state is VERY low. (+1) interpretation

(b) If the researcher wanted to have 40 percent ~~of his~~ pigment Z molecules in the excited state, at what temperature would he have to observe pigment Z (Assume he doesn't buy a new laser)?

P(excited state) = 0.40 (+2) right probabilities

P(ground state) = 0.60

$$\frac{P(\text{excited})}{P_{\text{ground}}} = \frac{0.40}{0.60} = \frac{e^{-\frac{E_{ex}}{kT}}}{e^{-\frac{E_{grd}}{kT}}} = e^{-\frac{(E_{ex}-E_{ground})}{kT}} = e^{-\frac{(6.626\times10^{-34})(6.3}{(1.38\times10^{-23})T}}$$

(+1) right equation (+2) plugging in #s

8 pts total

(+2) taking ln

$$\ln\left(\frac{0.4}{0.6}\right) = \frac{-(6.626\times10^{-34})(6.38\times10^{15})}{1.38\times10^{-23} \quad T} = -\frac{3.06\times10^{5}}{T}$$

$$-.405 = -\frac{3.06\times10^{5}}{T}$$

$$\boxed{T = 7.56\times10^{5}\ \text{K}}$$

(+1) getting right answer

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3. (18 pts) While on a research expedition to Don Juan Lake in Antarctica, you take a water sample for analysis at the base camp. The staff chemist finds that it is primarily dissolved $CaCl_2$ (MW=110.98 g/mol). You also notice that it freezes at -48 °C. (We're not making this up, it's true!) For this problem, please assume that ΔH and ΔS are independent of temperature and that $CaCl_2$ ionizes completely in water.

(9pt) a) What are the mole fractions (assume ideal solutions) of water, Ca^{2+}, and Cl^-? Assume that you <u>cannot</u> use the linear relationship $\Delta T = K_f\, m$, since this is a high concentration. Molar fusion of water is 6.007 kJ/mol, and pure water freezes at 273 K.

(1pt) $$\ln a_{H_2O} = \left(\frac{\Delta H_{fus}}{R}\right)\left(\frac{1}{T_0} - \frac{1}{T_f}\right)$$

[for rearrange/substitution] (2pt) $$a_{H_2O} \overset{\text{ideal}}{\cong} X_{H_2O} = \mathrm{Exp}\left[\frac{6.007\ \mathrm{kJ/mol}}{8.315\times10^{-3}\ \mathrm{kJ/mol{\cdot}K}}\left(\frac{1}{273\,K} - \frac{1}{225\,K}\right)\right]$$

(2pt) $$X_{H_2O} = 0.5686$$

(2pt) $$X_{Ca^{2+}} = \frac{1}{3}(1 - X_{H_2O}) = 0.1438$$

(2pt) $$X_{Cl^-} = \frac{2}{3}(1 - X_{H_2O}) = 0.2876$$

(8 pt) b) What is the osmotic pressure of a sample from Don Juan Lake against pure water at Antarctic temperatures (263 K)? If you didn't get part a, assume a_{H_2O} = 0.5. (Molarity of water at 263K is 55.6 mol/L).

$\boxed{\text{(1pt)}\ \ \Pi = cRT \longleftarrow \text{not valid due to high concentration.}}$

(2pt) $$\ln a_{H_2O} = \frac{-\Pi \bar{V}_A}{RT} \longrightarrow \text{(3pt)}\ \ \Pi = -\frac{RT}{\bar{V}_A}\ln a_{H_2O}$$

(3pt) $$\Pi = -\frac{(0.08205\ \mathrm{L{\cdot}atm/mol{\cdot}K})(263\,K)}{(1\,L/55.6\,mol)}\ln(0.5686) = 677.4\ \mathrm{atm}$$

or $$\Pi = -\frac{(0.08205\ \mathrm{L{\cdot}atm/mol{\cdot}K})(263\,K)}{(1\,L/55.6\,mol)}\ln(0.50) = 831.6\ \mathrm{atm}$$

(1pt) c) The osmotic pressure of cytoplasm inside a typical cell is 12.7 atm against pure water. What will happen to a cell placed in Don Juan Lake? (one sentence only).

Solute concentration is lower inside cell, ∴ water will flow out and cell will shrivel up.

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4. (10 pts) Short Questions:

A mole of He gas (MW He = 2 g/mol) has speeds which are distributed by the Maxwell-Boltzmann distribution, which we designate as P(u).

a) How would you find the average value of u^{20} ($\langle u^{20} \rangle$)? Set up, but DO NOT SOLVE, this problem.

+2

$$\langle u^{20} \rangle = \int_0^\infty u^{20} P(u)\, du$$

b) What is $\int_0^\infty P(u)du$? = probability of a molecule having a speed between 0 and ∞

+2

= 1

c) Would the mean speed of F_2 (MW F = 19 g/mol) gas be higher or lower than that of He gas at the same temperature?

+2

$\langle u \rangle = \sqrt{\frac{8kT}{\pi m}} \Rightarrow \langle u \rangle \propto \frac{1}{\sqrt{m}}$, so as mass increases, speed decreases. Mean speed of F_2 is lower.

The free-energy change of transferring pure water from the ocean to a freshwater drinking reservoir is:

+2

(a) positive
(b) negative
(c) not enough information is given

Transfering pure water from high concentration to low concentration is not spontaneous.

You put a dialysis bag full of a solution of negatively charged protein into 1 M NaCl(aq). The dialysis membrane is only permeable to water and ions. You allow these solutions to come to equilibrium.

Which of the following is true? (you may circle more than one)

+2

(a) There is a higher concentration of Na^+ ions inside the bag than outside the bag.
(b) There is a higher concentration of Cl^- ions outside the bag than inside the bag.
(c) There will a higher concentration of Na^+ ions outside the bag than inside the bag.

Negatively charged protein attracts Na^+ and repels Cl^-, resulting in skewed concentration of both ions.